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Preparation and Characterization of Chitosan Hybrid Membranes Containing Polyethylacrylate and Polybutylacrylate

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Abstract Chitosan hybrid membranes were prepared in the presence of polyethylacrylate and polybutylacrylate and characterized by measuring stress, strain, Young's modulus, swelling behavior and antibacterial properties against gram-negative and gram-positive bacteria using IR spectroscopy and scanning electron microscopy (SEM). The results show that the mechanical properties of the hybrid membranes were enhanced using polybutylacrylate. SEM images showed homogeneity of the prepared membranes. The swelling degree was of the order chitosan > chitosan/polyethylacrylate > chitosan/polybutylacrylate. Antibacterial properties of the hybrid membranes with polybutylacrylate and polyethylacrylate were higher than those of chitosan membranes without any additives.

Keywords Chitosan · Antimicrobial · Hybrid membrane · Polyethylacrylate · Polybutylacrylate

Introduction

Natural polymers are considered a promising alternative as they are biodegradable and renewable materials, keeping in mind the increased environmental regulations and strong requirements for an economy dependent on fossil resources (Arvanityannis 1999). Among the most important natural polymers, chitosan is one of the most studied materials for use in drug-delivery systems (Hu et al. 2004) as membranes for ultrafiltration, evaporation and reverse osmosis (Chanachai et al. 2000).

Chitosan—poly[β-(1–4)-2-amino-2-deoxy-D-glucopyranose]—is prepared by alkaline treatment of chitin and occurs naturally in some fungi, but its occurrence is much less frequent than chitin (Roberts 1992). Chitin is the second most important natural polysaccharide after cellulose. It presents in animals, particularly in crustaceans and insects, where it is an important constituent of the exoskeleton, and in certain fungi, where it is the principal febrile polymer in the cell wall (Hudson and Smith 1998). Chitin is poly[β-(1–4)-2-acetamido-2-deoxy-D-glucopyranose]. Thus, it is structurally similar to cellulose except that the (2)-hydroxyl group of cellulose is replaced by an acetamido group.

Chitosan is inexpensive, is nontoxic and has potentially reactive amino groups. Its potential use has been shown in many different fields, e.g., as an antifungal compound in agriculture, a flocculating agent in wastewater treatment, a food additive in the food industry, a hydrating agent in cosmetics and more recently a pharmaceutical agent in biomedicine (Rybicki and Szosland 1999; Muzzarelli 1977). Fibers are prepared from chitosan and chitin by dissolving the polymer in a solvent and coagulating the solution in a bath by the wet-spinning process (Rathke and Hudson 1994). Chitosan fibers can be used in many fields of application, such as the manufacture of wound dressing, sanitary fibrous materials, surgical threads, artificial limbs, textile materials for wastewater treatment and fibrous carriers for bioactive substances (Muzzarelli 1977).

Currently, chitosan is receiving a great deal of interest for medical and pharmaceutical applications (Fouda 2008; Hon 1996). The main reason for this increasing attention is certainly its intrinsic biocompatibility, which allows its use in many medical applications, e.g., as a carrier for drug-delivery

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systems, biomedical materials, blood anticoagulants, antitumor and antiviral agents, anticholesterol agents and ointments and to accelerate wound healing (Rybicki and Szosland 1999). Chitosan has antioxidant activity, scavenging ability to hydroxyl ions and chelating ability toward ferrous ions and may be used as a source of antioxidants (Ming-Tsung et al. 2008). Some undesired mechanical properties of chitosan, such as severe shrinkage, deformation after drying and compressibility at high operating pressure, as well as its inherent brittleness and stiffness limit its application and processing convenience (Francis and Matthew 2000).

Modifications of chitosan with polymers have been markedly investigated to tailor its properties to satisfy the basic requirements for particular applications. This can be accomplished by physical blending, chemical grafting or cross-linking (Zeng and Fang 2004). For instance, incorporation of polyethylene glycol into chitosan to improve swelling properties and blood compatibility has been investigated for biomedical applications (Amiji 1995). Chitosan grafted with acrylonitrile or methylmethacrylate using potassium persulfate as an initiator was studied for feasible use in packaging materials (Prashanth and Tharanathan 2003); the effect of glutaraldehyde as a cross-linking agent in the packaging application was studied as well (Tual et al. 2000).

The aim of the present study was to prepare and characterize hybrid chitosan membranes containing polyethylacrylate and polybutylacrylate and determine the effect of the presence of these polymers on the mechanical properties, swelling properties, water and air permeability, surface properties as well as antibacterial properties of chitosan membranes. We applied the formulations used to prepare these membranes to gauze fabrics to determine their effect on the antibacterial properties of gauze fabric.

Experimental Procedures

Materials

Chitosan of high molecular weight (6×10^5) was kindly supplied by Fluke Chemie (Buchs, Switzerland). Acetic acid, polyethylacrylate, polybutylacrylate and all other chemicals were of laboratory grade.

Methods

Preparation of Chitosan and Hybrid Chitosan Membranes

Chitosan membranes were prepared by dissolving chitosan in 1% acetic acid as solvent. Polyethylacrylate and polybutylacrylate (10% of the weight of chitosan) were added to chitosan solution. The obtained solution was caste on a glass plate and left overnight. The membranes were washed several times with distilled water.

Treatment of Gauze Fabric

Gauze fabrics were immersed in the formulations containing the same components used to prepare the hybrid membranes, padded to pick up 100% and dried at 100°C for 10 min; finally, the gauze fabrics were washed thoroughly with distilled water.

Analysis

Mechanical Properties

Young's modulus, stress yield, stress at rupture, strain at yield and strain at rupture were determined using an electronic tensile testing machine (Zwick 1425; Zwick, Ulm, Germany).

Scanning Electron Microscopy

Samples were examined by a JEOL–840X scanning electron microscope (SEM) (JEOL, Tokyo, Japan), magnification range 35–10,000, resolution 200 Å, acceleration voltage 19 kV. All samples were coated with gold before SEM testing.

FTIR Spectroscopy

FTIR spectroscopy was measured using the FTIR–Raman (model Nexus 670; Nicollet, Madison, WI). The spectral range was 400–4,000 cm^{-1}.

Antibacterial Activity

Antibacterial activity of chitosan membranes Escherichia coli DSMZ 498 and *Micrococcus luteus* AATCC 9341 were used as examples of gram-negative and gram-positive bacteria, respectively. One well-isolated colony was transferred aseptically, using a wire loop, to a 50-ml conical flask containing 25 ml SI medium. The flask was incubated at 37°C for 24 h, and then the grown bacteria were diluted with sterile saline to a final working concentration. Bacterial activity of chitosan membranes was evaluated by measuring the dehydrogenase activity (TTC test method) (Seidler 1991; Fouda 2008).

Density

The density of the prepared membranes was measured by multiplying the weight of 1 m^2 by the thickness in meters.

Air Permeability

Air permeability was measured according to ASTM-D-737 (1996).

Water Swelling Properties

The swelling behavior of the membranes was determined by equilibrium swelling studies, according to Shanmugasundaram et al. (2001). Dried samples were cut into small pieces (1 × 1 cm), precisely weighed and submerged in distilled water for different periods of time at room temperature until equilibrium was reached. At each immersion interval, the swollen samples were removed from water, wiped of excess water on the surface with filter paper and immediately weighed. The initial sample weight before immersion was recorded as W_d and the sample weight after each immersion interval was recorded as W_S. The percent swelling at equilibrium, E_{SW}, was calculated according to the swelling formula:

$$E_{SW} = (W_S - W_d)/W_d \times 100$$

Table 1 Sample comparison

Samples	Weight (g/m^2)	Thickness (mm)	Air permeability ($cm^3/cm^2/s$)	Pore size (μ)	Density (g/cm^3)
1	70	0.06	0	0	1.166
2	68	0.07			0.97
3	52	0.065			0.8

Sample 1 1% chitosan in 1% acetic acid, *sample 2* 1% chitosan in 1% acetic acid in the presence of 10% polyethylacrylate (on the weight of chitosan), *sample 3* 1% chitosan in 1% acetic acid in the presence of 10% polybutylcrylate (on the weight of chitosan)

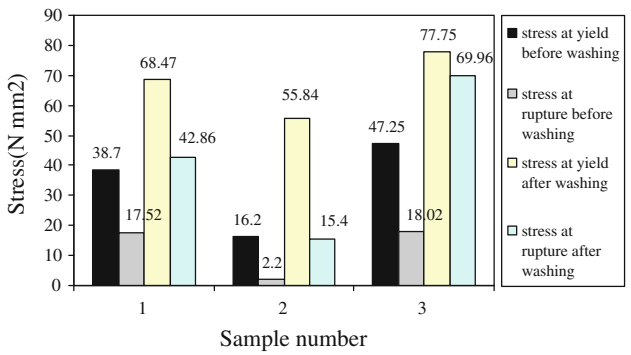

Fig. 1 Effect of polyethylacrylate and polybutylacrylate on stress properties. *1* 1% chitosan in 1% acetic acid, *2* 1% chitosan in 1% acetic acid in the presence of 10% polyethylacrylate (of the weight of chitosan), *3* 1% chitosan in 1% acetic acid in the presence of 10% polybutylcrylate (of the weight of chitosan)

Results and Discussion

Physical and Mechanical Properties of the Prepared Membranes

Table 1 shows the weight, thickness, air permeability and density of the prepared membranes. Table 1 shows that the three membranes (chitosan, chitosan/polyethylacrylate and chitosan/polybutylacrylate) have almost the same thickness but different weight and different density. It is clear also from Table 1 that the membranes have no air permeability.

Figure 1 shows the effect of polyethylacrylate and polybutylacrylate on the properties of chitosan membranes. It is clear from Fig. 1 that addition of polybutylacrylate to the formulation of chitosan membranes leads to increased stress properties of the prepared hybrid membranes. This holds true after washing the membranes with ethanolic solution of 1% sodium carbonate, but the values of stress

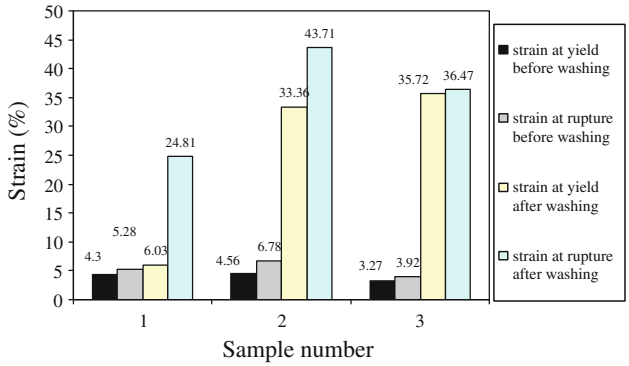

Fig. 2 Effect of polyethylacrylate and polybutylacrylate on strain properties. *1* 1% chitosan in 1% acetic acid, *2* 1% chitosan in 1% acetic acid in the presence of 10% polyethylacrylate (of the weight of chitosan), *3* 1% chitosan in 1% acetic acid in the presence of 10% polybutylcrylate (of the weight of chitosan)

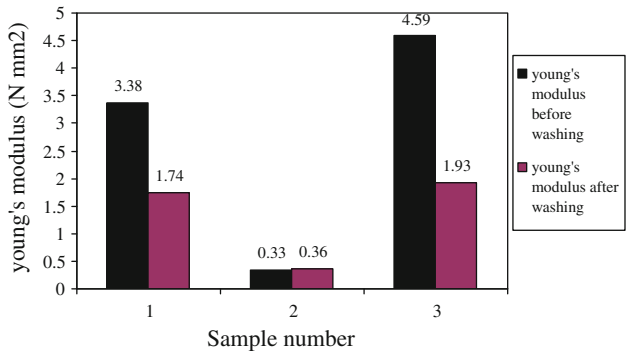

Fig. 3 Effect of polyethylacrylate and polybutylacrylate on Young's modulus. *1* 1% chitosan in 1% acetic acid, *2* 1% chitosan in 1% acetic acid in the presence of 10% polyethylacrylate (of the weight of chitosan), *3* 1% chitosan in 1% acetic acid in the presence of 10% polybutylcrylate (of the weight of chitosan)

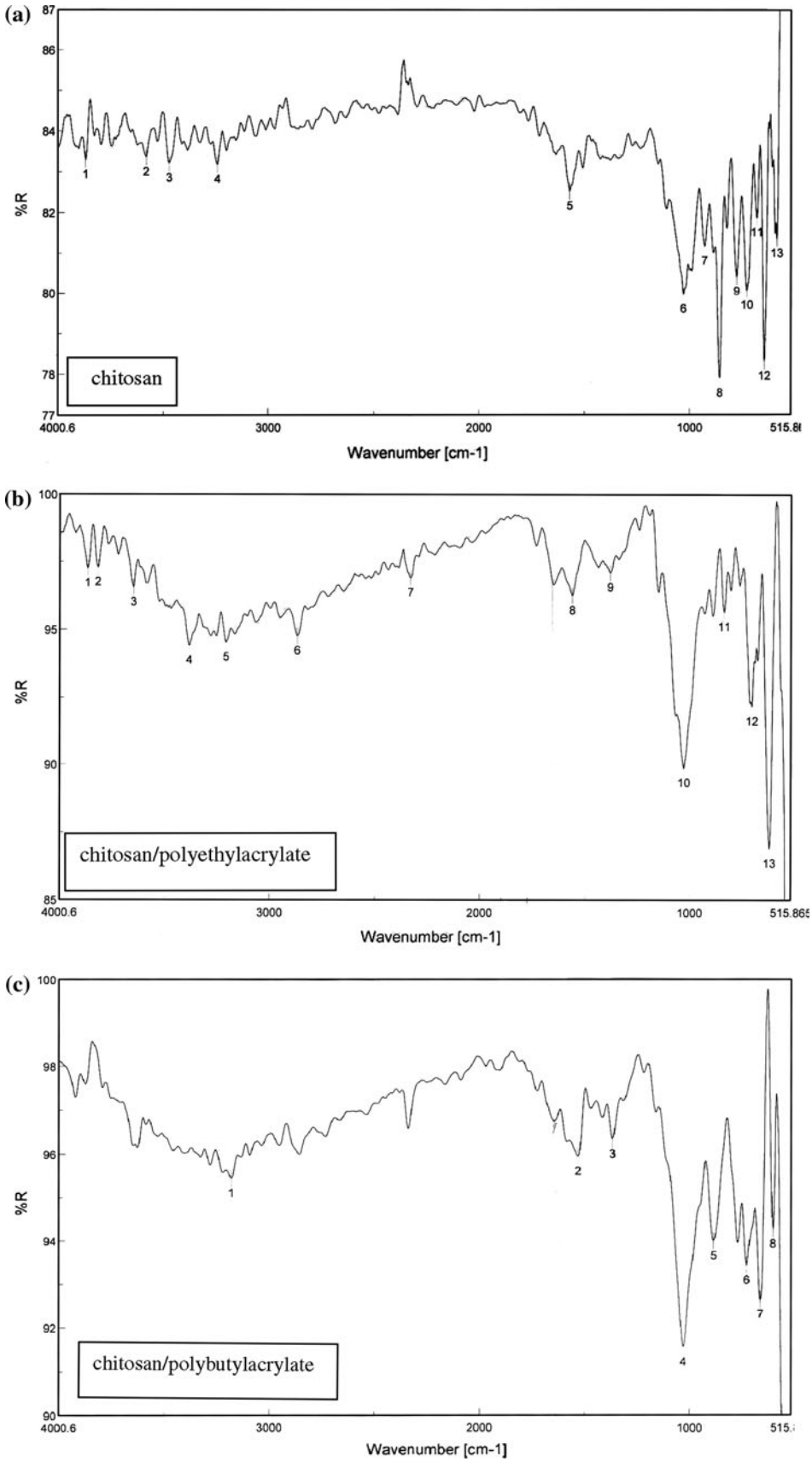

Fig. 4 IR spectra of hybrid membranes

before washing were lower than those after washing with the alcoholic solution of sodium carbonate. On the contrary, polyethylacrylate had an adverse effect on the stress properties of chitosan membranes before and after washing with the alcoholic solution of sodium carbonate, but still the stress values after washing with alcoholic solution of sodium carbonate were higher than those before washing.

Figure 2 reveals the effect of addition of polybutylacrylate and polyethylacrylate on the strain properties of chitosan membranes. It can be seen from Fig. 2 that addition of polybutylacrylate and polyethylacrylate to the membrane formulations had almost no effect on the strain properties before washing with alcoholic sodium carbonate solution. Washing with alcoholic sodium carbonate solution led to increased strain properties of membranes containing polybutylacrylate or polyethylacrylate.

Figure 3 shows the effect of addition of polybutylacrylate and polyethylacrylate to chitosan membrane formulations on Young's modulus. Figure 3 shows that addition of polyethylacrylate had an adverse effect on Young's modulus of chitosan membranes while polybutylacrylate enhanced Young's modulus of chitosan membranes before and after washing with the alcoholic solution of sodium carbonate.

The results of stress and strain properties as well as Young's modulus can be explained by the ability of these mixtures (chitosan, polyethylacrylate and/or polybutylacrylate) to form different types of hydrogen bonds, some intermolecular and others intramolecular, that may crosslink the blend. Also, the results after washing with alcoholic sodium carbonate can be attributed to the ability of sodium carbonate to neutralize acetic acid and the deposition of chitosan, which may affect the results of stress, strain and Young's modulus.

Overall, the results of stress, strain and Young's modulus indicate that chitosan membranes containing 10% polybutylacrylate have enough elasticity and strength to be used in different applications, especially before washing with alcoholic sodium carbonate.

FTIR of Chitosan Membranes

The FTIR spectra of chitosan, chitosan/polyethylacrylate and chitosan/polybutylacrylate membranes are shown in Fig. 4. The three spectra are almost similar. There are some differences, such as increasing the intensity of the peak at 1,650 cm^{-1} which attributed to the C=O of ester groups present in the structure of polyethylacrylate and polybutylacrylate. It is clear also from Fig. 4 that increasing the intensity of the peak at 2,868 cm^{-1} corresponds to CH_2 of polyethylacrylate and polybutylacrylate.

Swelling Behavior

Figure 5 exhibits the swelling behavior of chitosan membrane and chitosan hybrid membranes containing polyethylacrylate and polybutylacrylate with time. The swelling capacity of the membranes follows the order chitosan > chitosan/polyethylacrylate > chitosan/polybutylacrylate.

Figure 5 presents the swelling equilibrium results. The pure chitosan membrane achieved equilibrium after immersion for about 2 h in distilled water, and the maximum degree of swelling was 87%. The chitosan hybrid membranes with polyethylacrylate and polybutylacrylate reached equilibrium after about 2 h also but with maximum degrees of swelling of about 75 and 60%, respectively. This can be explained by increasing the intermolecular and intramolecular hydrogen bonds between chitosan and both polybutylacrylate and polyethylacrylate, which closes the structure and decreases the degree of membrane swelling.

SEM

Figure 6 shows SEM images of the chitosan membrane and the chitosan/polyethylacrylate and chitosan/polybutylacrylate hybrid membranes. These membranes show homogeneity between chitosan and the two polymers used as well as the absence of pores in the membrane structures.

Antibacterial Properties of Chitosan Membranes and Treated Gauze Fabrics

The antibacterial properties of chitosan and chitosan hybrid membranes against *M. luteus* (gram-positive bacteria) and

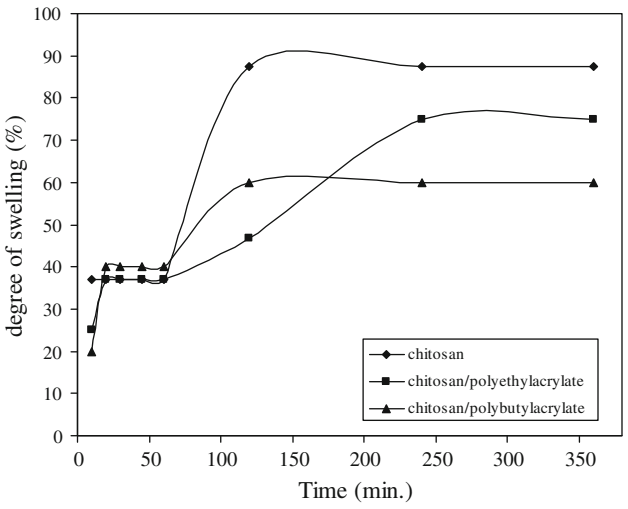

Fig. 5 Swelling behavior

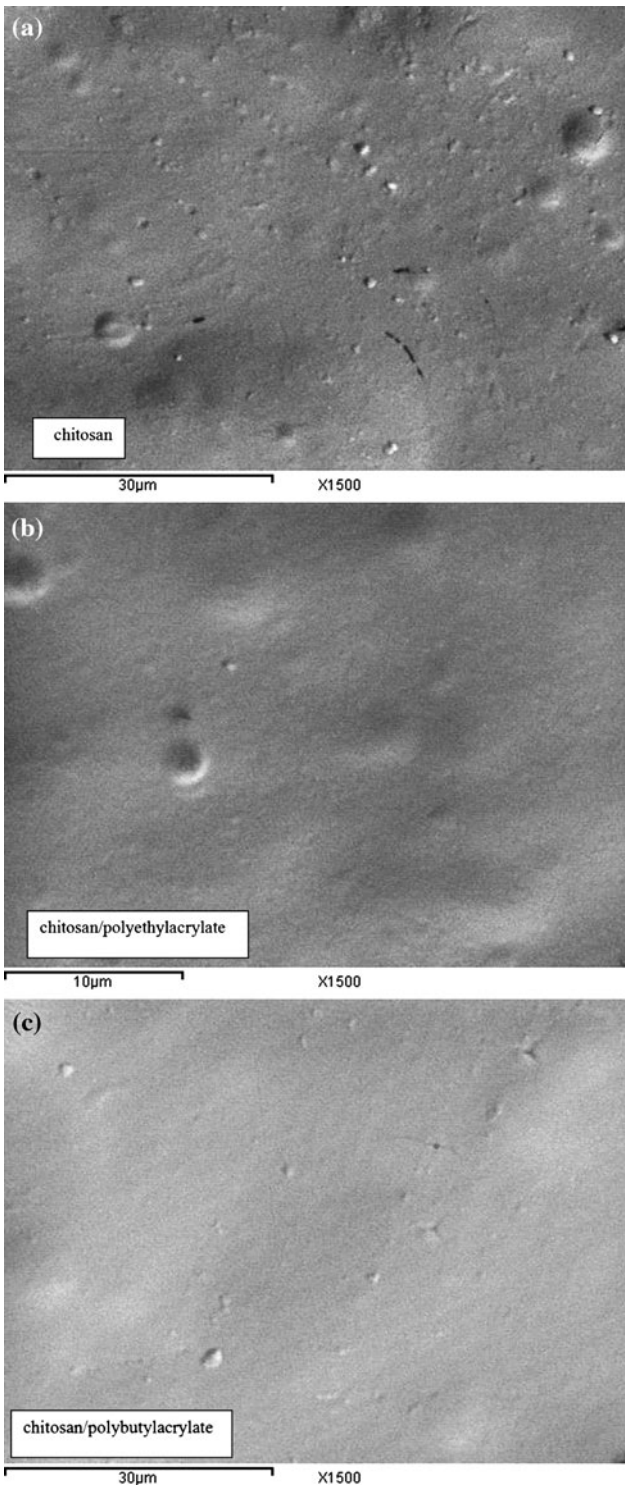

Fig. 6 SEM images of chitosan membranes

E. coli (gram-negative bacteria) are shown in Fig. 7. Figure 7 shows that chitosan membranes containing polyethylacrylate and polybutylacrylate have TTC values lower (higher antibacterial properties) than chitosan membrane alone, which means that the addition of polyethylacrylate and polybutylacrylate enhanced the antibacterial properties

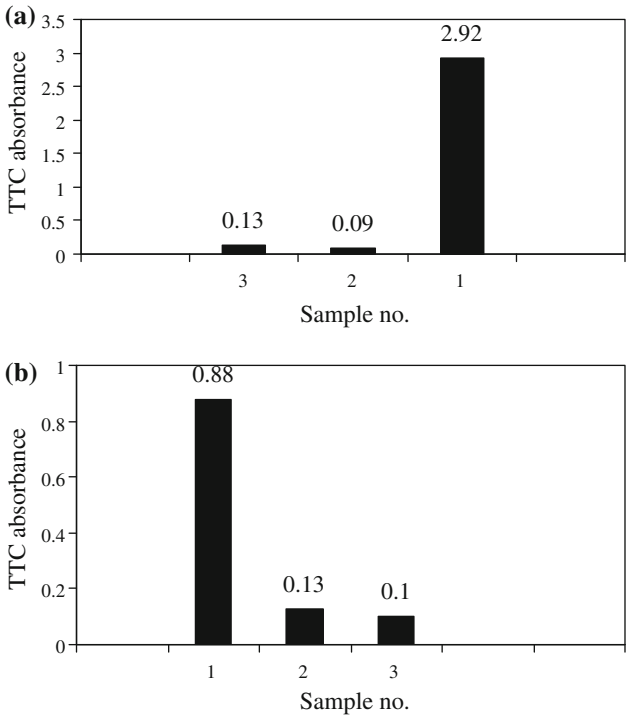

Fig. 7 Antibacterial properties against *M. luteus* and *E. coli*

of chitosan membranes against both gram-negative and gram-positive strains. There is almost no difference between the antibacterial properties of chitosan membranes containing polybutylacrylate and those of membranes containing polyethylacrylate. The antibacterial properties of the gauze fabrics were higher than those of untreated fabrics and had the same trend as the membranes against both types of bacteria, that is the gauze fabrics treated with chitosan in presence of polybutylacrylate and polyethylacrylate exhibit antibacterial properties higher than the gauze fabrics treated with chitosan only against both types of bacteria.

Conclusion

Chitosan membranes were prepared by addition of polybutylacrylate and polyethylacrylate. These membranes were characterized by measuring stress, strain, Young's modulus, swelling behavior and antibacterial properties against gram-negative and gram-positive bacteria using IR spectroscopy and SEM. From the results it can be concluded that the presence of polybutylacrylate leads to membranes with better strength and elasticity compared to membranes with polyethylacrylate. The swelling behavior was of the order chitosan > chitosan/polyethylacrylate > chitosan/polybutylacrylate. SEM images showed the homogeneity of the membranes prepared. The antibacterial properties against gram-negative and gram-positive bacteria were enhanced using polybutylacrylate and polyethylacrylate.

Gauze fabrics treated with the same formulations used to prepare the hybrid membranes exhibited higher antibacterial properties than untreated gauze fabrics.

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